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(54) **METHODS OF FORMING A CUTTING ELEMENT FOR AN EARTH-BORING TOOL, A RELATED CUTTING ELEMENT, AND AN EARTH-BORING TOOL INCLUDING SUCH A CUTTING ELEMENT**

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CPC B01J 3/06; B23B 27/20; E21B 10/00; C09K 3/14; B24D 3/00

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(56) **References Cited**

U.S. PATENT DOCUMENTS

3,696,875	A	10/1972	Cortes
3,894,673	A	7/1975	Lowder et al.
3,949,263	A	4/1976	Harper
4,018,576	A	4/1977	Lowder et al.
4,156,329	A	5/1979	Daniels et al.
4,225,322	A	9/1980	Knemeyer
4,228,942	A	10/1980	Dietrich
4,278,914	A	7/1981	Harper
4,319,707	A	3/1982	Knemeyer
4,340,650	A	7/1982	Pattanaik et al.

(Continued)

FOREIGN PATENT DOCUMENTS

DE	3337240	A1	5/1985
EP	3116	A1	10/1982

(Continued)

OTHER PUBLICATIONS

International Search Report for International Application No. PCT/US2012/055843, dated Mar. 28, 2013, 3 pages.

(Continued)

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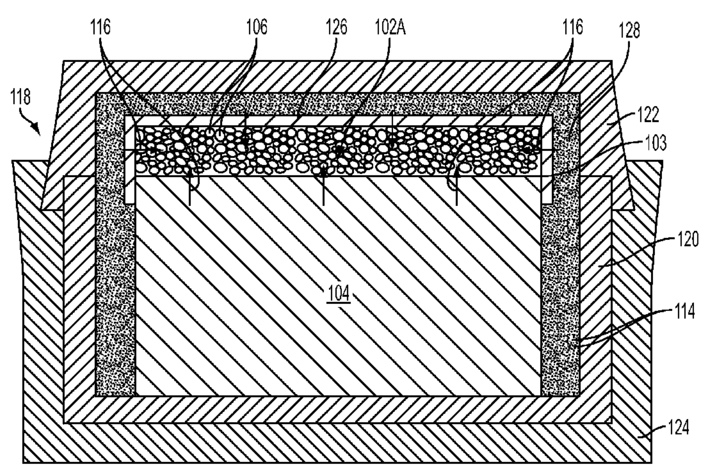
(57) **ABSTRACT**

A method of forming a cutting element for an earth-boring tool. The method includes providing diamond particles on a supporting substrate, the volume of diamond particles comprising a plurality of diamond nanoparticles. A catalyst-containing layer is provided on exposed surfaces of the volume of diamond nanoparticles and the supporting substrate. The diamond particles are processed under high temperature and high pressure conditions to form a sintered nanoparticle-enhanced polycrystalline compact. A cutting element and an earth-boring tool including a cutting element are also disclosed.

17 Claims, 6 Drawing Sheets



(56) **References Cited**

U.S. PATENT DOCUMENTS

4,359,112	A	11/1982	Garner et al.
4,381,825	A	5/1983	Radtke
4,539,018	A	9/1985	Whanger
4,560,853	A	12/1985	Ziegel
4,561,215	A	12/1985	Slimhauser et al.
4,593,776	A	6/1986	Salesky et al.
4,649,992	A	3/1987	Green et al.
4,661,180	A	4/1987	Frushour
4,676,124	A	6/1987	Fischer
4,689,276	A	8/1987	Jacquez
4,708,496	A	11/1987	McPherson
4,724,913	A	2/1988	Morris
4,732,364	A	3/1988	Seger et al.
4,764,036	A	8/1988	Mcphersen
4,766,040	A	8/1988	Hillert et al.
4,767,050	A	8/1988	Flood et al.
4,778,730	A	10/1988	Zucker
4,883,500	A	11/1989	Deakins et al.
4,884,476	A	12/1989	Okuzumi et al.
4,894,917	A	1/1990	Nicolson
4,908,046	A	3/1990	Wiand
4,919,220	A	4/1990	Fuller et al.
4,919,974	A	4/1990	McCune et al.
4,931,069	A	6/1990	Wiand
4,931,363	A	6/1990	Slutz et al.
4,932,582	A	6/1990	Une
4,943,488	A	7/1990	Sung et al.
4,945,686	A	8/1990	Wiand
4,993,505	A	2/1991	Packer et al.
5,030,276	A	7/1991	Sung et al.
5,049,164	A	9/1991	Horton et al.
5,092,083	A	3/1992	Raffaelli
5,100,045	A	3/1992	Wiand
5,115,697	A	5/1992	Rodriguez et al.
5,154,550	A	10/1992	Ilsobe et al.
5,161,335	A	11/1992	Tank
5,197,651	A	3/1993	Nakamura et al.
5,199,832	A	4/1993	Meskin et al.
5,213,171	A	5/1993	Clench et al.
5,239,746	A	8/1993	Goldman
5,259,148	A	11/1993	Wiand
5,282,513	A	2/1994	Jones
5,299,214	A	3/1994	Nakamura et al.
5,317,839	A	6/1994	Anderson
5,341,890	A	8/1994	Cawthorne et al.
5,342,129	A	8/1994	Dennis et al.
5,366,522	A	11/1994	Nakamura et al.
5,370,299	A	12/1994	Tanabe et al.
5,371,407	A	12/1994	Goldman
5,379,853	A	1/1995	Lockwood et al.
5,392,982	A	2/1995	Li
5,413,689	A	5/1995	de Nora Vittorio et al.
5,429,199	A	7/1995	Sheirer et al.
5,431,239	A	7/1995	Tibbitts et al.
5,435,815	A	7/1995	Ikegaya et al.
5,443,337	A	8/1995	Katayama
5,453,041	A	9/1995	Oliver
5,454,751	A	10/1995	Wiand et al.
5,456,329	A	10/1995	Dennis et al.
5,492,771	A	2/1996	Lowder et al.
5,498,081	A	3/1996	Dennis et al.
5,500,248	A	3/1996	Iacovangelo
5,505,273	A	4/1996	Azar
5,507,528	A	4/1996	Mastrosimone et al.
5,516,027	A	5/1996	Tanabe et al.
5,523,158	A	6/1996	Kapoor et al.
5,529,805	A	6/1996	Iacovangelo et al.
5,533,582	A	7/1996	Tibbitts
5,547,121	A	8/1996	Kapoor et al.
5,567,522	A	10/1996	Tanabe et al.
5,567,525	A	10/1996	Kapoor et al.
5,584,045	A	12/1996	Tanabe et al.
5,596,813	A	1/1997	Olson et al.
5,641,921	A	6/1997	Dennis et al.
5,647,878	A	7/1997	Iacovangelo et al.
5,653,376	A	8/1997	Nakamura et al.
5,653,378	A	8/1997	Olson et al.
5,656,045	A	8/1997	Wiand
5,709,279	A	1/1998	Dennis
5,738,698	A	4/1998	Kapoor et al.
5,762,660	A	6/1998	Makowiecki et al.
5,874,175	A	2/1999	Li et al.
5,951,378	A	9/1999	Miller et al.
5,976,206	A	11/1999	Bigelow et al.
6,042,463	A	3/2000	Johnson et al.
6,044,920	A	4/2000	Massa et al.
6,045,029	A	4/2000	Scott et al.
6,054,693	A	4/2000	Barmatz et al.
6,068,072	A	5/2000	Besson et al.
6,105,694	A	8/2000	Scott
6,109,918	A	8/2000	Hammond et al.
6,129,145	A	10/2000	Yamamoto et al.
6,155,755	A	12/2000	Kanada et al.
6,193,593	B1	2/2001	Miller et al.
6,209,185	B1	4/2001	Scott
6,211,463	B1	4/2001	Fabis
6,213,380	B1	4/2001	Collins et al.
6,213,931	B1	4/2001	Twardowski et al.
6,216,805	B1	4/2001	Lays et al.
6,224,473	B1	5/2001	Miller et al.
6,234,261	B1	5/2001	Evans et al.
6,302,225	B1	10/2001	Yoshida et al.
6,325,709	B1	12/2001	Nanda et al.
6,350,184	B1	2/2002	Holzapfel
6,358,624	B1	3/2002	Yoshida et al.
6,368,198	B1	4/2002	Sung et al.
6,374,932	B1	4/2002	Brady
6,376,268	B1	4/2002	Verdiell
6,464,393	B2	10/2002	Tatoh
6,489,634	B1	12/2002	Schaffer et al.
6,511,700	B1	1/2003	Airoldi et al.
6,524,357	B2	2/2003	Baldoni et al.
6,528,159	B1	3/2003	Kanada et al.
6,575,350	B2	6/2003	Evans et al.
6,671,965	B2	1/2004	Clemens et al.
6,725,953	B2	4/2004	Truax et al.
6,868,755	B2	3/2005	Yabuki et al.
6,889,890	B2	5/2005	Yamazaki et al.
6,902,808	B2	6/2005	Pinneo
6,915,794	B2	7/2005	Tommasini
6,949,873	B2	9/2005	Sung
7,011,134	B2	3/2006	Sung
7,132,309	B2	11/2006	Sung
7,152,701	B2	12/2006	Butland et al.
7,331,845	B2	2/2008	Imai et al.
7,339,791	B2	3/2008	Hoover et al.
7,359,487	B1	4/2008	Newcome
7,396,086	B1	7/2008	Hall et al.
7,401,863	B1	7/2008	Hall et al.
7,407,012	B2	8/2008	Keshavan et al.
7,416,145	B2	8/2008	Hall et al.
7,487,849	B2	2/2009	Radtke
7,635,035	B1	12/2009	Bertagnolli et al.
2001/0002918	A1	6/2001	Tatoh
2001/0004946	A1	6/2001	Jensen
2001/0030067	A1	10/2001	Evans et al.
2001/0047891	A1	12/2001	Truax et al.
2002/0014041	A1	2/2002	Baldoni et al.
2002/0051848	A1	5/2002	Li
2002/0114963	A1	8/2002	Petkie
2002/0125048	A1	9/2002	Traux et al.
2002/0173252	A1	11/2002	Li
2003/0080177	A1	5/2003	Yamazaki et al.
2003/0106270	A1	6/2003	Baldoni et al.
2003/0118827	A1	6/2003	Pinneo
2003/0121159	A1	7/2003	Clemens et al.
2003/0121369	A1	7/2003	Yabuki et al.
2003/0155404	A1	8/2003	Pinneo
2003/0183368	A1	10/2003	Paradis et al.
2003/0211306	A1	11/2003	Pinneo
2004/0026983	A1	2/2004	McAlvain
2004/0031438	A1	2/2004	Sung
2004/0065484	A1	4/2004	McAlvain
2004/0066127	A1	4/2004	Sung

(56) **References Cited**

U.S. PATENT DOCUMENTS

2004/0105237	A1	6/2004	Hoover et al.	
2004/0107581	A1	6/2004	Clemens	
2004/0112359	A1	6/2004	Sung	
2004/0119161	A1	6/2004	Saito et al.	
2004/0124231	A1	7/2004	Hasz et al.	
2004/0134687	A1	7/2004	Radford et al.	
2004/0152045	A1	8/2004	Kachalon	
2004/0159471	A1	8/2004	Azar et al.	
2004/0194967	A1	10/2004	Jaensch	
2004/0238227	A1*	12/2004	Smith et al.	175/431
2004/0246551	A1	12/2004	Reijnen	
2004/0256624	A1	12/2004	Sung	
2005/0077091	A1	4/2005	Butland et al.	
2005/0252501	A1	11/2005	Powell	
2005/0260940	A1	11/2005	Palushaj	
2005/0282358	A1	12/2005	Di Cioccio et al.	
2006/0068358	A1	3/2006	Lowder et al.	
2006/0157285	A1	7/2006	Cannon et al.	
2006/0174823	A1	8/2006	Sung	
2006/0191723	A1	8/2006	Keshavan	
2006/0247769	A1	11/2006	Molz et al.	
2006/0254830	A1	11/2006	Radtke	
2006/0266558	A1	11/2006	Middlemiss et al.	
2006/0272571	A1	12/2006	Cho	
2006/0278441	A1	12/2006	Cooley et al.	
2007/0023206	A1	2/2007	Keshavan	
2007/0034147	A1	2/2007	Wort et al.	
2007/0034416	A1	2/2007	Cho et al.	
2007/0099549	A1	5/2007	Palushaj	
2007/0128986	A1	6/2007	Imai et al.	
2007/0151554	A1	7/2007	Song et al.	
2007/0157469	A1	7/2007	Schulz-Harder	
2007/0157670	A1	7/2007	Sung	
2007/0198096	A1	8/2007	Wort	
2007/0205023	A1	9/2007	Hoffmaster et al.	
2007/0215390	A1	9/2007	Azar et al.	
2007/0221406	A1	9/2007	Hall et al.	
2008/0011522	A1	1/2008	Hall et al.	
2008/0029312	A1	2/2008	Hall et al.	
2008/0035388	A1	2/2008	Hall et al.	
2008/0036269	A1	2/2008	Hall et al.	
2008/0041992	A1	2/2008	Hall	
2008/0085407	A1	4/2008	Cooley et al.	
2008/0106139	A1	5/2008	Hall et al.	
2008/0110638	A1	5/2008	Hall et al.	
2008/0135660	A1	6/2008	Hall et al.	
2008/0142276	A1	6/2008	Griffo et al.	
2008/0145528	A1	6/2008	Deng et al.	
2008/0160886	A1	7/2008	Palushaj	
2008/0176494	A1	7/2008	Palushaj	
2008/0206576	A1	8/2008	Qian et al.	
2008/0230278	A9	9/2008	Hoffmaster et al.	
2009/0078470	A1	3/2009	Lyons et al.	
2009/0090563	A1	4/2009	Voronin et al.	
2009/0152018	A1	6/2009	Sani	
2010/0186304	A1*	7/2010	Burgess et al.	51/309
2011/0023375	A1	2/2011	Sani et al.	
2011/0073380	A1	3/2011	DiGiovanni	
2011/0088954	A1	4/2011	DiGiovanni et al.	

FOREIGN PATENT DOCUMENTS

EP	213434	A1	3/1987
EP	117241	A1	5/1987
EP	117241	B1	5/1987
EP	140600	A2	8/1988
EP	140600	B1	8/1988
EP	290839	A2	11/1988
EP	337685	A2	10/1989
EP	365843	A1	5/1990
EP	238938	A1	7/1990
EP	238938	B1	7/1990
EP	297071	A1	3/1992
EP	297071	B1	3/1992
EP	319926	A2	7/1992
EP	319926	B1	7/1992
EP	244947	B1	12/1992
EP	534729	A2	3/1993
EP	560287	A1	9/1993
EP	413543	A2	10/1993
EP	413543	B1	10/1993
EP	351952	A2	4/1994
EP	351952	B1	4/1994
EP	458434	A2	9/1994
EP	619382	A1	10/1994
EP	378378	A1	1/1995
EP	378378	B1	1/1995
EP	477585	B1	1/1995
EP	435423	A2	3/1995
EP	435423	B1	3/1995
EP	328583	B1	8/1995
EP	443517	A2	9/1995
EP	443517	B1	9/1995
EP	517264	A1	9/1995
EP	517264	B1	9/1995
EP	439017	A1	12/1995
EP	439017	B1	12/1995
EP	534370	A1	5/1996
EP	534370	B1	5/1996
EP	567124	B1	9/1997
EP	541400	A2	3/1998
EP	932199	A2	7/1999
EP	953652	A1	11/1999
EP	694510	A2	4/2000
EP	694510	B1	4/2000
EP	932199	A3	8/2000
EP	521405	A1	4/2001
EP	521405	B1	4/2001
EP	811082	B1	5/2001
EP	541071	A1	10/2001
EP	541071	B1	10/2001
EP	807693	B1	10/2001
EP	1151825	A2	11/2001
EP	1170460	A2	1/2002
EP	718462	B1	4/2002
EP	577066	A1	9/2002
EP	577066	B1	9/2002
EP	931782	A1	9/2002
EP	931782	B1	9/2002
EP	1036913	A1	10/2002
EP	1036913	B1	10/2002
EP	1053984	A2	2/2003
EP	1053984	A3	2/2003
EP	1053984	B1	2/2003
EP	1302273	A2	4/2003
EP	1314505	A1	5/2003
EP	1323502	A2	7/2003
EP	918134	A1	6/2004
EP	918134	B1	6/2004
EP	1323502	A3	6/2004
EP	1432029	A2	6/2004
EP	1302273	A3	7/2004
EP	1432029	A3	8/2004
EP	1079063	A1	9/2004
EP	1452685	A2	9/2004
EP	940215	A1	1/2005
EP	940215	B1	1/2005
EP	1452685	A3	3/2005
EP	1516942	A1	3/2005
EP	1151825	B1	6/2006
EP	1430007	B1	9/2006
EP	1302273	B1	3/2008
EP	1323502	B1	10/2008
EP	1976004	A1	10/2008
GB	1310686	A	3/1973
GB	1310883	A	3/1973
GB	1462510	A	1/1977
GB	1489130	A	10/1977
GB	2169687	A	7/1986
GB	2209483	A	5/1989
GB	2211856	A	7/1989
GB	2213414	A	8/1989
GB	2224225	A	5/1990

(56) **References Cited**

FOREIGN PATENT DOCUMENTS

GB	2259263	A	3/1993
GB	2267733	A	12/1993
GB	2268768	A	1/1994
GB	2276896	A	10/1994
GB	2285823	A	7/1995
GB	2287897	A	10/1995
GB	2298665	A	9/1996
GB	2339713	A	2/2000
GB	2353053	A	2/2001
GB	2353545	A	2/2001
GB	2398316	A	8/2004
GB	2404405	A	2/2005
GB	2404406	A	2/2005
GB	2405424	A	3/2005
GB	2420139	A	5/2006
GB	2424433	A	9/2006
GB	2426223	A	11/2006
GB	2429727	A	3/2007
GB	2438073	A	11/2007
GB	2453135	A	4/2009
GB	2453663	A	4/2009
JP	56088325	A	7/1981
JP	59156669	A	9/1984
JP	60187603	A	9/1985
JP	61135121	A	6/1986
JP	62139865	A	6/1987
JP	63024002	A	2/1988
JP	63300803	A	12/1988
JP	01096073	A	4/1989
JP	01225774	A	9/1989
JP	01275746	A	11/1989
JP	02137679	A	5/1990
JP	02274405	A	11/1990
JP	03033095	A	2/1991
JP	03198360	A	8/1991
JP	03221374	A	9/1991
JP	04096340	A	3/1992
JP	04331798	A	11/1992
JP	05139890	A	6/1993
JP	05140769	A	6/1993
JP	05228624	A	9/1993
JP	05299478	A	11/1993
JP	06016498	A	1/1994
JP	06047531	A	2/1994
JP	06205857	A	7/1994
JP	07138093	A	5/1995
JP	08039361	A	2/1996
JP	08039362	A	2/1996
JP	09201705	A	8/1997
JP	10118914	A	5/1998
JP	10202530	A	8/1998
JP	10242221	A	9/1998
JP	10340934	A	12/1998
JP	11008274	A	1/1999
JP	11045915	A	2/1999
JP	1168037	A	6/1999
JP	200024932	A	1/2000
JP	2000178082	A	6/2000
JP	2001127375	A	5/2001
JP	2001192801	A	7/2001
JP	2001210613	A	8/2001
JP	2002154058	A	5/2002
JP	2002169539	A	6/2002
JP	2002263831	A	9/2002
JP	2003117682	A	4/2003
JP	2003165056	A	6/2003
JP	2003205479	A	7/2003
JP	2004188518	A	7/2004
JP	2004291126	A	10/2004
JP	2005325417	A	11/2005
JP	2008093772	A	4/2008
JP	2008128924	A	6/2008
WO	8707342	A1	12/1987
WO	8801702	A1	3/1988
WO	8809826	A1	12/1988
WO	9201092	A1	1/1992
WO	9302823	A1	2/1993
WO	9325494	A1	12/1993
WO	9610466	A1	4/1996
WO	9626303	A1	8/1996
WO	9705757	A1	2/1997
WO	9806564	A1	2/1998
WO	9845091	A2	10/1998
WO	9904128	A2	1/1999
WO	9928084	A1	6/1999
WO	9929465	A1	6/1999
WO	9935694	A1	7/1999
WO	0034001	A1	6/2000
WO	0116051	A1	3/2001
WO	0126153	A1	4/2001
WO	0136711	A1	5/2001
WO	0161399	A1	8/2001
WO	0202844	A2	1/2002
WO	0207183	A1	1/2002
WO	02058143	A2	7/2002
WO	03027043	A3	4/2003
WO	2005010245	A1	2/2005
WO	2005027799	A1	3/2005
WO	2005075142	A1	8/2005
WO	2005084879	A1	9/2005
WO	2005113198	A2	12/2005
WO	2005122284	A2	12/2005
WO	2005122284	A3	8/2006
WO	2006116214	A1	11/2006
WO	2007007126	A1	1/2007
WO	2007074720	A1	7/2007
WO	2008086280	A1	7/2008
WO	2008087610	A1	7/2008
WO	2008088908	A1	7/2008
WO	2009010934	A2	1/2009
WO	2009013716	A2	1/2009
WO	2009044488	A1	4/2009

OTHER PUBLICATIONS

International Written Opinion for International Application No. PCT/US2012/055843, dated Mar. 19, 2014, 6 pages.

International Preliminary Report on Patentability for International Application No. PCT/US2012/055843, dated Mar. 25, 2014, 7 pages.

International Search Report for International Application No. PCT/US2012/055843, dated Feb. 28, 2013, 3 pages.

International Written Opinion for International Application No. PCT/US2012/055843, dated Feb. 28, 2013, 6 pages.

* cited by examiner

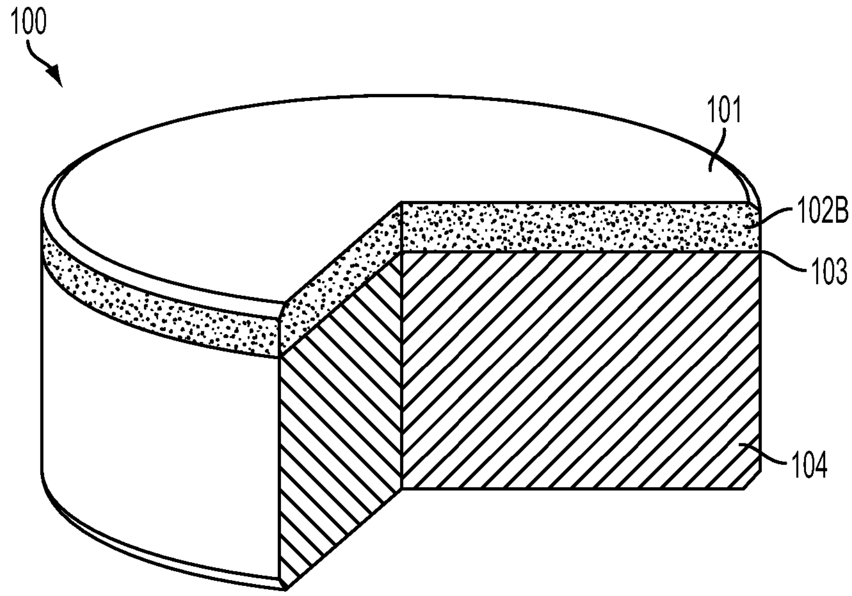


FIG. 1

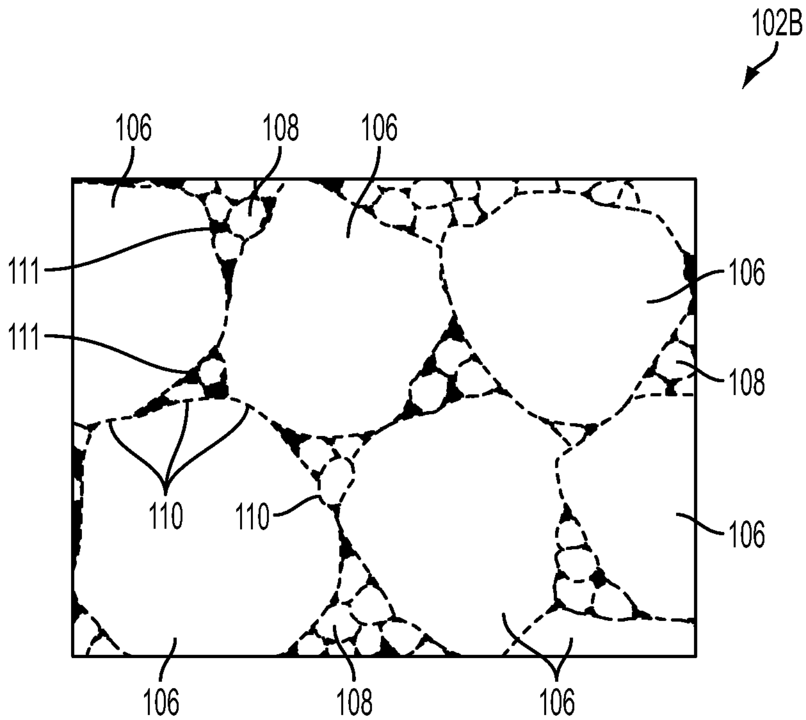


FIG. 2

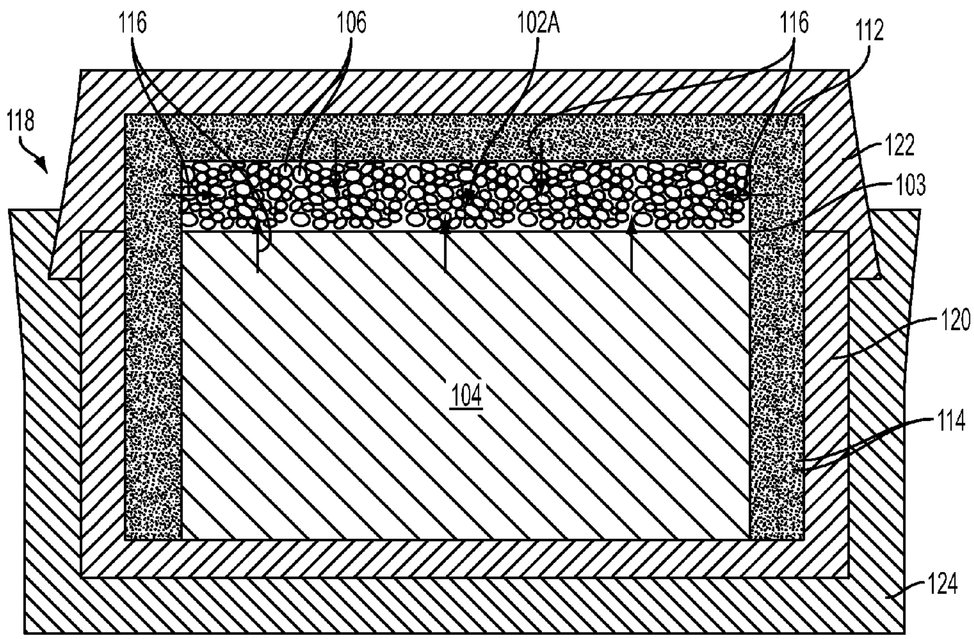


FIG. 3

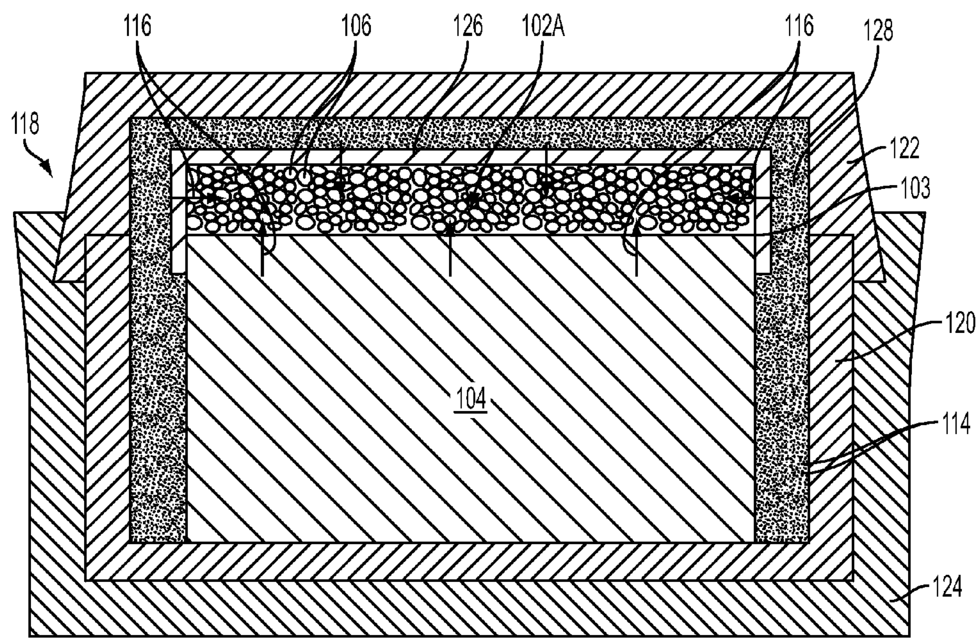


FIG. 4

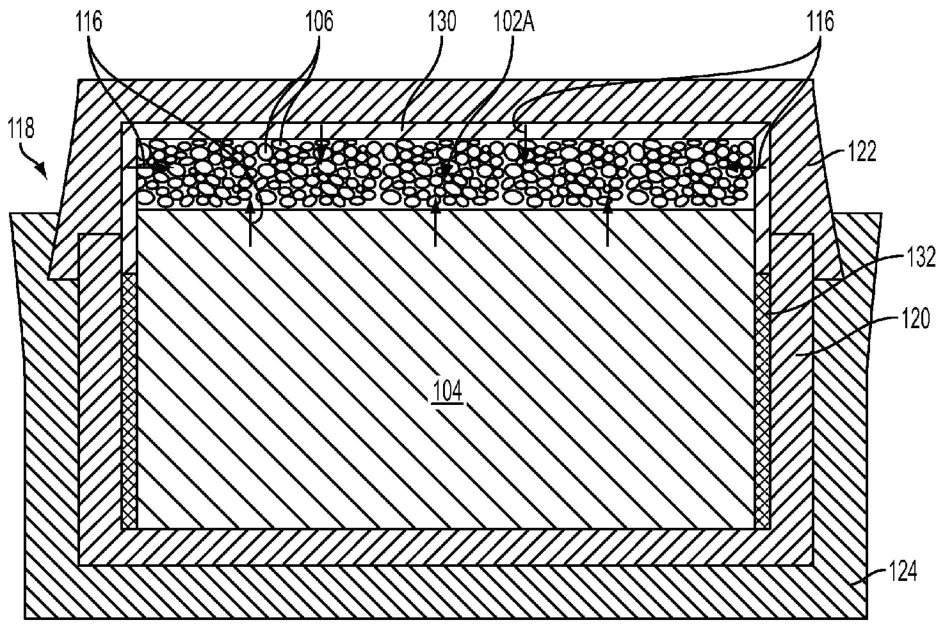


FIG. 5

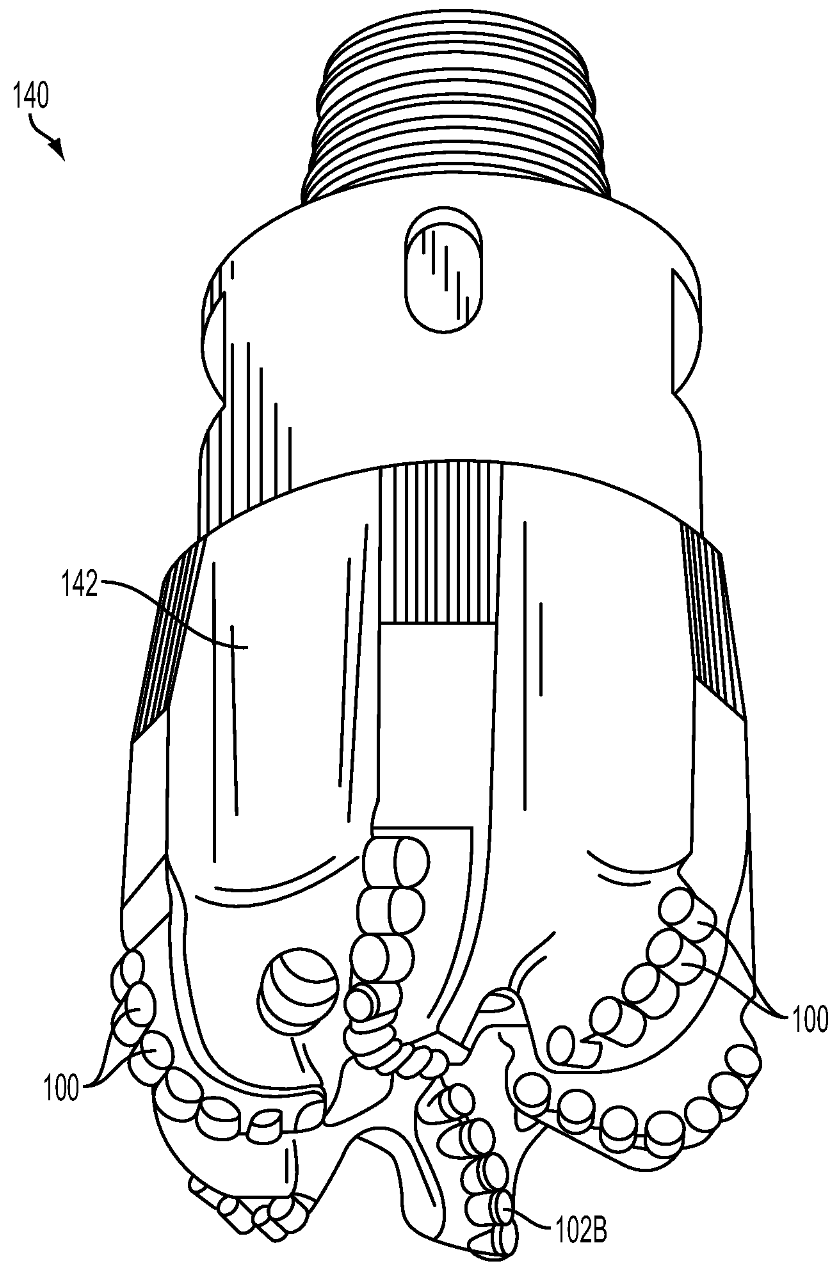


FIG. 6

METHODS OF FORMING A CUTTING ELEMENT FOR AN EARTH-BORING TOOL, A RELATED CUTTING ELEMENT, AND AN EARTH-BORING TOOL INCLUDING SUCH A CUTTING ELEMENT

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Patent Application Ser. No. 61/536,443, filed Sep. 19, 2011, the disclosure of which is hereby incorporated herein in its entirety by this reference.

TECHNICAL FIELD

Embodiments of the disclosure relate to methods of forming a cutting element for an earth-boring tool, to a related cutting element, and to an earth-boring tool including such a cutting element.

BACKGROUND

Earth-boring tools for forming wellbores in subterranean earth formations may include a plurality of cutting elements secured to a body. For example, fixed-cutter earth-boring rotary drill bits ("drag bits") include a plurality of cutting elements that are fixedly attached to a bit body of the drill bit. Similarly, roller cone earth-boring rotary drill bits may include cones that are mounted on bearing pins extending from legs of a bit body such that each cone is capable of rotating about the bearing pin on which it is mounted. A plurality of cutting elements may be mounted to each cone of the drill bit.

The cutting elements used in such earth-boring tools often include polycrystalline diamond compacts ("PDC"), which act as cutting faces of a polycrystalline diamond ("PCD") material. PCD material is material that includes inter-bonded grains or crystals of diamond material. In other words, PCD material includes direct, inter-granular bonds between the grains or crystals of diamond material. The terms "grain" and "crystal" are used synonymously and interchangeably herein.

PDC cutting elements are generally formed by sintering and bonding together relatively small diamond (synthetic, natural or a combination) grains, termed "grit," under conditions of high temperature and high pressure in the presence of a catalyst (e.g., cobalt, iron, nickel, or alloys and mixtures thereof) to form a layer (e.g., a compact or "table") of PCD material. These processes are often referred to as high temperature/high pressure (or "HTHP") processes. The supporting substrate may comprise a cermet material (i.e., a ceramic-metal composite material) such as, for example, cobalt-cemented tungsten carbide. In some instances, the PCD material may be formed on the cutting element, for example, during the HTHP process. In such instances, catalyst material (e.g., cobalt) in the supporting substrate may be "swept" into the diamond grains during sintering and serve as a catalyst material for forming the diamond table from the diamond grains. Powdered catalyst material may also be mixed with the diamond grains prior to sintering the grains together in an HTHP process.

Upon formation of the diamond table using an HTHP process, catalyst material may remain in interstitial spaces between the inter-bonded grains of the PDC. The presence of the catalyst material in the PDC may contribute to thermal damage in the PDC when the PDC cutting element is heated during use due to friction at the contact point between the

cutting element and the formation. Accordingly, the catalyst material (e.g., cobalt) may be leached out of the interstitial spaces using, for example, an acid or combination of acids (e.g., aqua regia). Substantially all of the catalyst material may be removed from the PDC, or catalyst material may be removed from only a portion thereof, for example, from a cutting face of the PDC, from a side of the PDC, or both, to a desired depth. However, a fully leached PDC is relatively more brittle and vulnerable to shear, compressive, and tensile stresses than is a non-leached PDC. In addition, it is difficult to secure a completely leached PDC to a supporting substrate.

To improve the thermal stability, the mechanical durability, and bonding characteristics of the PDC, nanoparticles (e.g., particles having an average particle diameter of about 500 nm or less) may be provided in the interstitial spaces of the PDC. However, disadvantageously, as higher concentrations of nanoparticles are incorporated into the interstitial spaces, the "sweep" of catalyst material from the supporting substrate during subsequent HTHP processing is inhibited, resulting in formation of a nanoparticle-enhanced ("nanoparticle-enhanced") PDC that may be poorly sintered at positions distal from an interface of the nanoparticle-enhanced PDC and the supporting substrate.

BRIEF SUMMARY

In some embodiments, the disclosure includes a method of forming a cutting element for an earth-boring tool. Diamond particles may be provided on a supporting substrate, the volume of diamond particles comprising a plurality of diamond nanoparticles. A catalyst-containing layer may be provided on exposed surfaces of the volume of diamond nanoparticles and the supporting substrate. The diamond particles may be processed under high temperature and high pressure conditions to form a sintered nanoparticle-enhanced polycrystalline compact.

In additional embodiments, the disclosure includes a cutting element for use in an earth-boring tool. The cutting element may comprise a sintered nanoparticle-enhanced polycrystalline compact formed by a method comprising providing a volume of diamond particles on a supporting substrate, the volume of diamond particles comprising a plurality of diamond nanoparticles. The diamond particles may be processed under high temperature and high pressure conditions to form a sintered nanoparticle-enhanced polycrystalline compact. The diamond particles may be processed under high temperature and high pressure conditions to form the sintered nanoparticle-enhanced polycrystalline compact.

In yet additional embodiments, the disclosure includes an earth-boring tool comprising a cutting element. The cutting element may comprise a sintered nanoparticle-enhanced polycrystalline compact formed by a method comprising providing a volume of diamond particles on a supporting substrate, the volume of diamond particles comprising a plurality of diamond nanoparticles. The diamond particles may be processed under high temperature and high pressure conditions to form a sintered nanoparticle-enhanced polycrystalline compact. The diamond particles may be processed under high temperature and high pressure conditions to form the sintered nanoparticle-enhanced polycrystalline compact.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

FIG. **1** is a partial cut-away perspective view of an embodiment of a cutting element for an earth-boring tool, in accordance with an embodiment of the disclosure;

FIG. **2** is a simplified cross-sectional view illustrating how a microstructure of the sintered nanoparticle-enhanced polycrystalline compact of the cutting element of FIG. **1** may appear under magnification;

FIG. **3** is a simplified cross-sectional view of a configuration that may be used in a method of forming the cutting element of FIG. **1**, in accordance with an embodiment of the disclosure;

FIG. **4** is a simplified cross-sectional view of a configuration that may be used in a method of forming the cutting element of FIG. **1**, in accordance with another embodiment of the disclosure;

FIG. **5** is a simplified cross-sectional view of a configuration that may be used in a method of forming the cutting element of FIG. **1**, in accordance with yet another embodiment of the disclosure;

FIG. **6** is a perspective view of an embodiment of a fixed-cutter earth-boring rotary drill bit including cutting elements such as that shown in FIG. **1**.

DETAILED DESCRIPTION

The illustrations presented herein are, in some instances, not actual views of any particular cutting element insert, cutting element, drill bit, system or method, but are merely idealized representations which are employed to describe embodiments of the disclosure. Additionally, elements common between figures may retain the same numerical designation.

Embodiments of the disclosure include methods for forming a cutting element including a nanoparticle-enhanced polycrystalline compact, such as a nanoparticle-enhanced polycrystalline diamond compact ("PDC"), along with related cutting elements, and earth-boring tools including such cutting elements. The methods of the disclosure utilize at least one catalyst material to form the polycrystalline compact.

As used herein, the term "inter-granular bond" means and includes any direct atomic bond (e.g., covalent, metallic, etc.) between atoms in adjacent grains of hard material.

As used herein, the term "nanoparticle" means and includes any particle having an average particle diameter of about 500 nm or less. Nanoparticles include grains in a polycrystalline material having an average grain size of about 500 nm or less.

As used herein, the term "polycrystalline material" means and includes any material comprising a plurality of grains or crystals of the material that are bonded directly together by inter-granular bonds. The crystal structures of the individual grains of the material may be randomly oriented in space within the polycrystalline material.

As used herein, the term "nanoparticle-enhanced polycrystalline compact" means and includes any structure including a polycrystalline material and plurality of nanoparticles, wherein the polycrystalline material is formed by a process that involves application of pressure (e.g., compression) to a precursor material or materials used to form the polycrystalline material.

As used herein, the term "catalyst material" refers to any material that is capable of substantially catalyzing the formation of inter-granular bonds between grains of hard material during an HTHP but at least contributes to the degradation of the inter-granular bonds and granular material under elevated temperatures, pressures, and other conditions that may be encountered in a drilling operation for forming a wellbore in a subterranean formation. For example, catalyst materials for diamond include cobalt, iron, nickel, other elements from Group VIIIA of the Periodic Table of the Elements, and alloys thereof.

As used herein, the term "hard material" means and includes any material having a Knoop hardness value of about 3,000 Kg_f/mm^2 (29,420 MPa) or more. Hard materials include, for example, diamond and cubic boron nitride.

FIG. **1** illustrates a cutting element **100**, which may be formed in accordance with embodiments of methods as disclosed herein. The cutting element **100** includes a sintered nanoparticle-enhanced polycrystalline compact **102**B bonded to supporting substrate **104** at an interface **103**. The sintered nanoparticle-enhanced polycrystalline compact **102**B includes a cutting surface **101**. Although the cutting element **100** in the embodiment depicted in FIG. **2** is cylindrical or disc-shaped, in other embodiments, the cutting element **100** may have any desirable shape, such as a dome, cone, or chisel.

Referring to FIG. **2**, the sintered nanoparticle-enhanced polycrystalline compact **102**B may include interspersed and inter-bonded grains that form a three-dimensional network of polycrystalline material. The grains of the sintered nanoparticle-enhanced polycrystalline compact **102**B may have a multimodal grain size distribution. For example, the sintered nanoparticle-enhanced polycrystalline compact **102**B may include larger grains **106** and smaller grains **108**. Direct inter-granular bonds between the larger grains **106** and the smaller grains **108** are represented in FIG. **2** by dashed lines **110**.

The larger grains **106** may be formed of and include a hard material (e.g., diamond, boron nitride, silicon nitride, silicon carbide, titanium carbide, tungsten carbide, tantalum carbide). The larger grains **106** may be monodisperse, wherein all the larger grains **106** are of substantially the same size, or may be polydisperse, wherein the larger grains **106** have a range of sizes and are averaged. The smaller grains **108** may be nanoparticles formed of and including at least one of hard material (e.g., diamond, boron nitride, silicon nitride, silicon carbide, titanium carbide, tungsten carbide, tantalum carbide) and non-hard material (e.g., carbides, ceramics, oxides, intermetallics, clays, minerals, glasses, elemental constituents, and various forms of carbon, such as carbon nanotubes, fullerenes, adamantanes, graphene, and amorphous carbon). The smaller grains **108** may be monodisperse, wherein all the smaller grains **108** are of substantially the same size, or may be polydisperse, wherein the smaller grains **108** have a range of sizes and are averaged. The sintered nanoparticle-enhanced polycrystalline compact **102**B may include from about 0.01% to about 99% by volume or weight smaller grains **108**, such as from about 0.01% to about 50% by volume smaller grains **108**, or from 0.1% to about 10% by weight smaller grains **108**.

Interstitial spaces **111** (shaded black in FIG. **2**) are present between the inter-bonded larger grains **106** and smaller grains **108** of the sintered nanoparticle-enhanced polycrystalline compact **102**B. The interstitial spaces **111** may be at least partially filled with a solid material, such as at least one of a catalyst material (e.g., iron, cobalt, nickel, or an alloy thereof) and a carbon-free material. In at least some embodiments, the solid material of the interstitial spaces **111** may vary throughout a thickness of the sintered nanoparticle-enhanced polycrystalline compact **102**B. For example, the interstitial spaces **111** proximate the interface **103** (FIG. **1**) of the supporting substrate **104** (FIG. **1**) and the sintered nanoparticle-enhanced polycrystalline compact **102**B may be filled with a first solid material (e.g., a catalyst material, such as cobalt) and the interstitial spaces **111** proximate exposed surfaces of the polycrystalline compact **102**, such as the cutting surface

101 (FIG. 1), may be filled with a second solid material (e.g., another catalyst material, such as nickel). At least some of the interstitial spaces 111 may be filled with a combination of the first solid material and the second solid material. In additional embodiments, the interstitial spaces 111 may comprise empty voids within the sintered nanoparticle-enhanced polycrystalline compact 102B in which there is no solid or liquid substance (although a gas, such as air, may be present in the voids). Such empty voids may be formed by removing (e.g., leaching) solid material out from the interstitial spaces 111 after forming the sintered nanoparticle-enhanced polycrystalline compact 102B. In yet further embodiments, the interstitial spaces 111 may be at least partially filled with a solid substance in one or more regions of the sintered nanoparticle-enhanced polycrystalline compact 102B, while the interstitial spaces 111 in one or more other regions of the sintered nanoparticle-enhanced polycrystalline compact 102B comprise empty voids.

An embodiment of the disclosure will now be described with reference to FIG. 3, which illustrates a simplified cross-sectional view of a configuration that may be used in a method of forming the cutting element 100 (FIG. 1). A volume of diamond particles 102A may be provided on a supporting substrate 104 within a canister 118. The diamond particles 102A may include diamond nanoparticles, and the diamond particles 102A may ultimately form the grains 106, 108 (FIG. 2) of diamond in a resulting nanoparticle-enhanced polycrystalline compact 102B (FIG. 2) to be formed by sintering the diamond particles 102A, as disclosed hereinbelow. A catalyst-containing layer 112 may be provided adjacent the volume of diamond particles 102A, as shown in FIG. 3. In some embodiments, the catalyst-containing layer 112 may also extend over one or more surfaces of the substrate 104.

As shown in FIG. 3, the canister 118 may encapsulate the diamond particles 102A, the supporting substrate 104, and the catalyst-containing layer 112. The canister 118 may include an inner cup 120, in which at least a portion of each of the diamond particles 102A, the supporting substrate 104, and the catalyst-containing layer 112 may each be disposed. The canister 118 may further include a top end piece 122 and a bottom end piece 124, which may be assembled and bonded together (e.g., swage bonded) around the inner cup 120 with the diamond particles 102A, the supporting substrate 104, and the catalyst-containing layer 112 therein. The sealed canister 118 then may be subjected to an HTHP process to sinter the diamond particles 102A and form the nanoparticle-enhanced polycrystalline compact 102B of the cutting element 100 (FIG. 1).

The supporting substrate 104 may include a material that is relatively hard and resistant to wear. By way of non-limiting example, the supporting substrate 104 may include a cemented carbide material, such as a cemented tungsten carbide material, in which tungsten carbide particles are cemented together in a metallic binder material. The metallic binder material may include, for example, catalyst material such as cobalt, nickel, iron, or alloys and mixtures thereof. The metallic binder material may be capable of catalyzing inter-granular bonds between the diamond particles 102A, as described in further detail below. In at least some embodiments, the supporting substrate 104 includes a cobalt-cemented tungsten carbide material.

The catalyst-containing layer 112 may include plurality of particles 114 comprising a catalyst material. The catalyst material may be any material capable of catalyzing inter-granular bonds between the unbonded nanoparticles and the inter-bonded larger grains 106 in the diamond particles 102A. As non-limiting examples, the catalyst material may comprise one or more of silicon, cobalt, iron, nickel, or an alloy or mixture thereof. By way of non-limiting example, the catalyst-containing layer 112 may comprise a layer of cobalt-cemented tungsten carbide particles, or a substantially solid layer of cobalt-cemented tungsten carbide material. The catalyst material in the catalyst-containing layer 112 may be the same as or different than a catalyst (e.g., cobalt or a cobalt alloy) in the supporting substrate 104. By way of non-limiting example, the catalyst material in the catalyst-containing layer 112 may be Ni, and the catalyst material in the substrate 104 may be Co. The catalyst-containing layer 112 may, optionally, also include a non-diamond carbon material such as graphite. The non-diamond carbon material may increase the amount of catalyst material that infiltrates or permeates the diamond particles 102A during HTHP processing (e.g., sintering) by pre-saturating the catalyst material with carbon.

With continued reference to FIG. 3, during subsequent HTHP processing, the catalyst material of the catalyst-containing layer 112 and catalyst material in the supporting substrate 104 may infiltrate or permeate the diamond particles 102A in the directions represented by directional arrows 116 in FIG. 3. The HTHP processing may enable inter-granular bonding between the unbonded diamond particles 102A to form the sintered nanoparticle-enhanced polycrystalline compact 1028 (FIG. 1) including the inter-bonded smaller grains 108 (FIG. 2) and larger grains 106.

The presence of the nanoparticles in the unbonded diamond particles 102A may impede the infiltration of catalyst material through an entirety of the unbonded diamond particles 102A solely from the substrate 104 in an HTHP process. Thus, in an effort to allow adequate infiltration of catalyst material through the entirety of the volume of the unbonded diamond particles 102A, the catalyst-containing layer 112 is provided adjacent the volume of the diamond particles 102A on one or more sides thereof that are not adjacent the substrate 104 so as to allow catalyst to infiltrate into the diamond particles 102A from more than one side of the volume of diamond particles 102A.

Another embodiment of the disclosure will now be described with reference to FIG. 4, which illustrates a simplified cross-sectional view of a configuration that may be used in method of forming the cutting element 100 (FIG. 1). Diamond particles 102A may be provided on supporting substrate 104 within the canister 118 (FIG. 3). A first catalyst-containing layer 126 may be provided on exposed surfaces of the diamond particles 102A and on at least a portion of exposed surfaces (e.g., exposed side surfaces) of the supporting substrate 104. A second catalyst-containing layer 128 may be provided on exposed surfaces of the first catalyst-containing layer 126 and on remaining exposed surfaces of the supporting substrate 104.

The second catalyst-containing layer 128 may be substantially similar to the catalyst-containing layer 112 (FIG. 3) described above. The first catalyst-containing layer 126 may be a solid layer, such as a film, sheet, or mesh. The first catalyst-containing layer 126 may include a catalyst material as described above that is capable of catalyzing inter-granular bonding between the unbonded diamond particles 102A. The catalyst material of the first catalyst-containing layer 126 may the same as or different than each of a catalyst material in the supporting substrate 104 and catalyst material of the second catalyst-containing layer 128. As shown in FIG. 4, the first catalyst-containing layer 126 may cover exposed surfaces of the volume of diamond particles 102A and may extend to cover a portion of exposed side surfaces of the supporting substrate 104 proximate the interface 103 of the diamond particles 102A and the supporting substrate 104. In additional embodiments, the first catalyst-containing layer **126** may cover more or less of the exposed surfaces of the supporting substrate **104**. For example, the first catalyst-containing layer **126** may at least substantially cover the exposed side surfaces of the supporting substrate **104**. In further embodiments, the first catalyst-containing layer **126** may cover more or less of the volume of diamond particles **102**A. For example, at least a portion of side surfaces of the volume of diamond particles **102**A may be left uncovered by the first catalyst-containing layer **126**.

With continued reference to FIG. **4**, during subsequent HTHP processing, the catalyst material of the first catalyst-containing layer **126**, the catalyst material of the second catalyst-containing layer **128**, and catalyst material (e.g., metal binder) in the supporting substrate **104** may infiltrate or permeate the diamond particles **102**A as represented by directional arrows **116**. The HTHP processing may enable inter-granular bonding between the diamond particles **102**A to form the sintered nanoparticle-enhanced polycrystalline compact **102**B (FIG. **1**) including the inter-bonded smaller grains **108** (FIG. **2**) and larger grains **106**.

Yet another embodiment of the disclosure will now be described with reference to FIG. **5**, which illustrates a simplified cross-sectional view of a configuration that may be used in method of forming the cutting element **100** (FIG. **1**). Diamond particles **102**A may be provided on supporting substrate **104** within the canister **118** (FIG. **3**). A catalyst-containing layer **130** may be provided on exposed surfaces of the volume of diamond particles **102**A and on at least a portion of exposed surfaces of the supporting substrate **104**. A non-catalyst-containing layer **132** may, optionally, be provided on remaining exposed surfaces (e.g., exposed side surfaces) of the supporting substrate **104**.

The catalyst-containing layer **130** may be substantially similar to the first catalyst-containing layer **126** (FIG. **4**) described above. The non-catalyst-containing layer **132**, if provided, may be a solid non-particulate layer, such as a film, sheet, or mesh. The non-catalyst-containing layer **132** may include a non-catalyst material, such as carbides, ceramics, oxides, intermetallics, clays, minerals, glasses, elemental constituents, and various forms of carbon (e.g., carbon nanotubes, fullerenes, adamantanes, graphene, and amorphous carbon). A thickness of the non-catalyst-containing layer **132** may be substantially the same as a thickness of the catalyst-containing layer **130**. As shown in FIG. **5**, the non-catalyst-containing layer **132** may cover a portion of exposed side surfaces of the supporting substrate **104** not covered by the catalyst-containing layer **130**. In additional embodiments, the non-catalyst-containing layer **132** may cover more or less of the exposed surfaces of the supporting substrate **104**. For example, the non-catalyst-containing layer **132** may at least substantially cover the exposed side surfaces of the supporting substrate **104** (e.g., when the catalyst-containing layer **130** covers less of the exposed side surfaces of the supporting substrate **104**, or when the catalyst-containing layer **130** covers no portion of the exposed side surfaces of the supporting substrate **104**). In further embodiments, the non-catalyst-containing layer **132** may cover at least a portion of the volume of diamond particles **102**A.

With continued reference to FIG. **5**, during subsequent HTHP processing, catalyst material of the catalyst-containing layer **130** and catalyst material in the supporting substrate **104** may infiltrate or permeate the diamond particles **102**A as represented by directional arrows **116**. The HTHP processing may enable inter-granular bonding between the diamond particles **102**A to form the sintered nanoparticle-enhanced polycrystalline compact **102**B (FIG. **1**) including the inter-bonded smaller grains **108** (FIG. **2**) and larger grains **106**.

In additional embodiments, the diamond particles **102**A may be replaced with a previously formed nanoparticle-enhanced polycrystalline compact (similar to the compact **102**B) in which catalyst material has previously been removed (e.g., leached) from interstitial spaces between the diamond grains therein, and which is desired to be bonded to the substrate **104** in an HTHP process. Such processes are often referred to in the art as "re-attach" processes.

Embodiments of cutting elements **100** (FIG. **1**) that include sintered nanoparticle-enhanced polycrystalline compact **102**B (FIG. **1**) as described herein may be secured to an earth-boring tool and used to remove subterranean formation material in accordance with additional embodiments of the present disclosure. The earth-boring tool may, for example, be a rotary drill bit, a percussion bit, a coring bit, an eccentric bit, a reamer tool, a milling tool, etc. As a non-limiting example, FIG. **6** illustrates a fixed-cutter type earth-boring rotary drill bit **140** that includes a plurality of cutting elements **100** (FIG. **1**), each of which includes a sintered nanoparticle-enhanced polycrystalline compact **102**B (FIG. **1**), as previously described herein. The rotary drill bit **140** includes a bit body **142**, and the cutting elements **100**, which include the sintered nanoparticle-enhanced polycrystalline compact **102**B, are bonded to the bit body **142**. The cutting elements **100** may be brazed, welded, or otherwise secured, within pockets formed in the outer surface of the bit body **142**.

Advantageously, as compared to previously known processes, the methods of the disclosure enable catalyst material to infiltrate or permeate a larger volume of diamond particles **102**A that include diamond nanoparticles during HTHP processing. As a result, the methods of the disclosure may be used to form cutting elements **100** including sintered nanoparticle-enhanced polycrystalline compacts **102**B more rapidly and uniformly, improving production efficiency and increasing the quality of the cutting elements **100** produced.

While the disclosure has been described herein with respect to certain example embodiments, those of ordinary skill in the art will recognize and appreciate that it is not so limited. Rather, many additions, deletions and modifications to the embodiments described herein may be made without departing from the scope of the invention as hereinafter claimed. In addition, features from one embodiment may be combined with features of another embodiment while still being encompassed within the scope of the invention as contemplated by the inventor. Further, the invention has utility in drill bits having different bit profiles as well as different cutter types.

What is claimed is:

1. A method of forming a cutting element for an earth-boring tool, comprising:

providing a volume of diamond particles on a supporting substrate, the volume of diamond particles comprising a plurality of diamond nanoparticles;

providing a catalyst-containing layer discrete from the volume of diamond particles on each of a top and sides of the volume of diamond particles; and

processing the volume of diamond particles under high temperature and high pressure conditions to form a sintered nanoparticle-enhanced polycrystalline compact.

2. The method of claim **1**, further comprising selecting the catalyst-containing layer to comprise a plurality of particles comprising a catalyst material.

3. The method of claim **1**, further comprising selecting the catalyst-containing layer to comprise a solid layer comprising a catalyst material.

4. The method of claim **1**, further comprising selecting the catalyst-containing layer to comprise at least one of cobalt, iron, and nickel.

5. The method of claim **1**, further comprising selecting the catalyst-containing layer to comprise cemented tungsten carbide.

6. The method of claim **1**, further comprising selecting the catalyst-containing layer to comprise a catalyst material and a non-diamond carbon material.

7. The method of claim **1**, further comprising selecting the catalyst-containing layer to comprise a catalyst material different than another catalyst material of the supporting substrate.

8. The method of claim **7**, wherein selecting the catalyst-containing layer to comprise a catalyst material different than another catalyst material of the supporting substrate comprises:

selecting the catalyst material to comprise at least one of cobalt, iron, and nickel; and

selecting the another catalyst material of the supporting substrate to comprise at least one other of cobalt, iron, and nickel.

9. A method of forming a cutting element for an earth-boring tool, comprising:

providing a volume of diamond supporting tin substrate, the volume of diamond particles comprising a plurality of diamond nanoparticles;

providing a catalyst-containing layer on exposed surfaces of each of the volume of diamond particles and the supporting substrate;

providing another catalyst-containing layer on the catalyst-containing layer; and

processing the volume of diamond particles under high temperature and high pressure conditions to form a sintered nanoparticle-enhanced polycrystalline compact.

10. The method of claim **9**, further comprising:

selecting the catalyst-containing layer to comprise a solid structure selected from the group consisting of a film, a sheet, and a mesh; and

selecting the another catalyst-containing layer to comprise a plurality of particles.

11. The method of claim **9**, further comprising selecting the catalyst-containing layer and the another catalyst-containing layer to comprise different catalyst materials.

12. The method of claim **9**, further comprising selecting at least two of the supporting substrate, the catalyst-containing layer, and the another catalyst-containing layer to comprise the same catalyst material.

13. A method of forming a cutting element for an earth-boring tool, comprising:

providing a volume of diamond particles on a supporting substrate, the volume of diamond articles comprising a plurality of diamond nanoparticles;

providing a catalyst-containing layer on exposed surfaces of the volume of diamond particles and on a portion of exposed side surfaces of the supporting substrate; and

processing the volume of diamond particles under hi hg temperature and high pressure conditions to form a sintered nanoparticle-enhanced polycrystalline compact.

14. The method of claim **13**, further comprising providing another catalyst-containing layer on the catalyst-containing layer and on remaining portions of the exposed side surfaces of the supporting substrate.

15. The method of claim **13**, further comprising providing a non-catalyst-containing layer on remaining portions of the exposed side surfaces of the supporting substrate.

16. The method of claim **15**, further comprising selecting the non-catalyst-containing layer to comprise at least one of a ceramic, a carbide, an oxide, an intermetallic, a clay, a mineral, a glass, carbon nanotubes, fullerene, adamantane, graphene, and amorphous carbon.

17. The method of claim **15**, wherein providing a non-catalyst-containing layer on remaining portions of the exposed side surfaces of the supporting substrate comprises forming the non-catalyst-containing layer to exhibit the same thickness as the catalyst-containing layer.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 9,194,189 B2
APPLICATION NO. : 13/611278
DATED : November 24, 2015
INVENTOR(S) : Anthony A. DiCiovanni et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the specification:

	COLUMN 6,	LINE 25,	change "compact **1028**" to --compact **102**B--

In the claims:

CLAIM 9,	COLUMN 9,	LINE 24,	change "diamond supporting tin substrate," to --diamond particles on a substrate,--
CLAIM 13,	COLUMN 10,	LINE 13,	change "diamond articles" to --diamond particles--
CLAIM 13,	COLUMN 10,	LINE 18,	change "particles under hi hg" to --particles under high--

Signed and Sealed this
Fifth Day of April, 2016

Michelle K. Lee

Michelle K. Lee
Director of the United States Patent and Trademark Office